

On the virial expansion of model adsorptive systems

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ABSTRACT

We investigate the thermodynamic properties of various super-critical model adsorptive systems with different fluid-solid attractive strengths using the confined-density virial expansion, with coefficients calculated using the Mayer-sampling Monte Carlo method up to fifth order. We find that the virial expansion converges for adsorptive systems over a density range corresponding approximately to the film-formation regime. Beyond this regime, higher order effects become increasingly important. The virial expansion of the density profile is also investigated. It is determined that this expansion gives insight into the structure associated with adsorption. We also find that weakly attractive systems have a more negative second virial coefficient than strongly attractive systems. This runs counter to the usual interpretation of bulk fluid virial coefficients. This is due to the infinite-dilution limit being very different for adsorbed fluids compared to bulk fluids.

1. Introduction

Gas adsorption in porous materials is important to a wide range of applications, such as gas storage, separations, and catalysis [1–5]. Experimental measurements to characterize the thermodynamics of pure-component adsorption is relatively well established, while a host of theoretical and computational methods, such as classical density functional theory and molecular simulation, connects intermolecular interactions to observable adsorption behavior. These computational approaches can be quite powerful and insightful and rely on an accurate description of the adsorbate-adsorbate and adsorbate-adsorbent interactions. The latter is captured by the Henry’s constant K_H , and physically corresponds to the Boltzmann weighted interaction between a single adsorbate molecule and the adsorbent. Moreover, knowledge of K_H provides the adsorption isotherm and other adsorptive properties in the infinite-dilution limit. Unfortunately, most applications do not operate in the infinite-dilution regime, and applying Henry’s law outside of this regime leads to crude and approximate predictions at best. Thus, it would be useful to predict adsorptive properties beyond the Henry’s law regime, using other measures that can be easily calculated or do not require computationally intensive simulation. To this end, we turn to the virial expansion.

The virial expansion provides a systematic means to incorporate increasingly complex (two-body, three-body, etc) interactions, and describe thermodynamic properties beyond the infinite-dilution limit. As such, the virial expansion plays an important role in the metrology of dilute bulk gases [6]. The virial expansion provides a direct link between the intermolecular interactions in a fluid and its thermodynamic properties [7, 8], and therefore virial coefficients can be used as a metric for characterizing fluids. In the case of a bulk fluid, the second virial coefficient is an experimentally measurable quantity that is directly related to the pairwise intermolecular forces between its constituent molecules. Thus, the second virial coefficient can be used to test the accuracy of intermolecular potentials. The reduced second virial coefficient can also be used as a parameter in corresponding states models for fluids with short ranged attractions [9]. All of these characteristics make the virial expansion an attractive framework to describe adsorptive thermodynamics.

While the application of the virial expansion to bulk fluids has a long and rich history, only comparatively recently has it been applied to inhomogeneous fluids. Note that there are several choices of independent variable when considering the virial expansion of inhomogeneous fluids. The series can be expressed in terms of the activity, the bulk fluid density in equilibrium with the fluid [10–12], the density profile [13], or the average fluid density in the inhomogeneous system [14], the last being the focus of this study. Because all of these expansions require calculating complex cluster integrals, early studies of the virial expansion of inhomogeneous systems only considered coefficients at second or third order, and considered repulsive systems [15–20], sticky spheres in repulsive pores [20], Lennard-Jones particles in repulsive pores [21], and attractive particles in attractive pores [22], for example. Coefficients up to fourth order have been calculated for hard spheres near a single repulsive wall [17], and in very narrow cylindrical pores [23].

More recently, Kofke et al. have developed the Mayer-sampling Monte Carlo (MSMC) technique to calculate virial coefficients up to high order [24]. This technique has been used to study hard spheres near a single wall [25, 26] and in slit-pores [27], for orders $n \leq 7$. In this work, we utilize the MSMC method to investigate the virial coefficients of attractive fluids in adsorptive (i.e. attractive) pores. We seek to address two main questions: 1) To what extent does the virial expansion build upon Henry’s law and 2) what physical insights does the virial expansion give to the thermodynamics of adsorptive systems? While these questions have been addressed to some degree previously, here we additionally study how variable fluid-solid attractive strength impacts the virial expansion of confined fluids. The paper is organized as follows. Section 2 provides the theoretical background to the Rowlinson virial expansion of confined fluids used in this study. Section 3 compares the Rowlinson expansion to the alternative Belleman expansion for confined fluids. Section 4 summarizes the several model fluids we considered. Section 5 outlines the simulation method used. Section 6 presents our main results. Section 7 discusses the context of our results. Finally, section 8 provides our main conclusions.

2. Background

As discussed above, there are several types of virial expansions for inhomogeneous confined systems, but we focus on the virial expansion of the confined grand potential in terms of the average confined density formulated by Rowlinson [14]. We consider a system of identical particles with pairwise-additive spherically-symmetric interactions, given by $u(i, j) = u(|\mathbf{r}_i - \mathbf{r}_j|)$, where \mathbf{r}_i is the position of particle i . In addition, we consider single body external fields of the form $\phi(i) = \phi(\mathbf{r}_i)$. We define the activity as $\alpha = \exp[\beta\mu]/\Lambda^3$, where μ is the chemical potential, Λ is the de Broglie wavelength, $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, and T is the temperature. We define the external field quantities $G = \int_V d\mathbf{r}_i \exp[-\beta\phi(i)]/V$ and $g(i) = \exp[-\beta\phi(i)]/G$, where V is a volume encompassing the system. We also define the reduced activity $z = \alpha G$. These definitions are nonstandard, but simplify the expressions below. With these definitions, we can write the grand potential, Ω , as

$$-\beta\Omega/V = \sum_{n=1} b_n z^n, \quad (1)$$

where b_n is the order n cluster integral. In general, these are given by

$$V n! b_n = \int_{\infty} d\mathbf{r}^n \gamma(\mathbf{r}^n) \prod_{i=1}^n g(i), \quad (2)$$

where $\gamma(\mathbf{r}^n)$ is the sum of all connected diagrams of n nodes connected with Mayer f-functions $f(i, j) = \exp[-\beta u(i, j)] - 1$. Note that, by definition, $b_1 = 1$. In the case of a bulk fluid, all external field factors are unity, and one degree of freedom can be integrated out leading to the bulk coefficient \tilde{b}_n (we use the tilde throughout this work to denote bulk properties) given in the usual form

$$n! \tilde{b}_n = \int_V d\mathbf{r}^{n-1} \gamma(\mathbf{r}^n). \quad (3)$$

Next, we consider the density virial expansion, given by

$$-\beta\Omega/V = \sum_{n=1} B_n \rho^n, \quad (4)$$

where $\rho = N/V$, with N being the number of particles in the system, is the fluid density. We note here that the definition of V is somewhat arbitrary in the presence of an external field as in the case of confining walls in a pore. The only requirement is that the definition of V must be consistent between all expressions. The coefficients B_n are easily related to the cluster integrals b_n . The density ρ is determined from Eq. (1) by differentiation with respect to the reduced activity z

$$\rho = -z \left(\frac{\partial \beta\Omega/V}{\partial z} \right)_{\beta, V} = \sum_{n=1} n b_n z^n. \quad (5)$$

Substitution of this expression into Eq. (4), equating to Eq. (1), and collecting like powers of z leads to the relationship between b_n and B_n of the form

$$B_n = (1 - n)b_n - R_n, \quad (6a)$$

where the factor R_n is given by

$$R_n = \sum_{\mathbf{m}} m! B_m \prod_{i=1}^n \frac{(i b_i)^{m_i}}{m_i!}, \quad (6b)$$

and $\sum_{\mathbf{m}}(\dots)$ is the sum over all vectors $\mathbf{m} = [m_1, \dots, m_{n-1}]$ such that

$$\begin{aligned} n &= \sum_{i=1}^n i m_i \\ m &= \sum_{i=1}^n m_i \end{aligned} \quad (6c)$$

$$1 < m < n.$$

Note that by definition, $B_1 = 1$ and $R_1 = 0$. We note that this is similar to the

generating equation presented in the literature previously [28]. However, those relationships cast B_n solely as a function of b_n or vice versa. In the case of a bulk fluid, the expression for B_n simplifies greatly. Specifically,

$$\tilde{B}_n = \frac{1-n}{n!} \int d\mathbf{r}^{n-1} \Gamma(\mathbf{r}^{n-1}) \quad (7)$$

where $\Gamma(\mathbf{r}^n)$ is the sum of all connected and irreducible diagrams with n nodes connected by Mayer f -function. Therefore, it is computationally simpler to calculate \tilde{B}_n directly for bulk fluids. With the presence of an external field, no such simplification occurs (due to the factors $g(i)$), and it is therefore simpler to calculate b_n from Eq. (3), and then calculate B_n using Eq. (6).

Other thermodynamic properties are easily calculated from the virial expansion. The Helmholtz free energy per particle can be expressed as the sum of ideal gas and excess contributions, $f = f^{\text{ex}} + f^{\text{ig}}$, where [29]

$$\begin{aligned} \beta f^{\text{ig}} &= \ln \left(\frac{\rho \Lambda^3}{G} \right) - 1, \\ \beta f^{\text{ex}} &= \sum_{n=2} \frac{1}{n-1} B_n \rho^{n-1}. \end{aligned} \quad (8)$$

The ideal gas reference state is composed of non-interacting particles in the external field $\phi(\mathbf{r})$. The chemical potential, i.e., the derivative of the Helmholtz free energy with respect to particle number N , is therefore

$$\begin{aligned} \beta \mu^{\text{ig}} &= \ln \left(\frac{\rho \Lambda^3}{G} \right), \\ \beta \mu^{\text{ex}} &= \sum_{n=2} \frac{n}{n-1} B_n \rho^{n-1}. \end{aligned} \quad (9)$$

The chemical potential can also be found by noting that $\beta \Omega / N = \beta f - \beta \mu$ for a single component fluid. Henry's law can be recovered by considering the confined liquid at the same chemical potential as a bulk liquid in the limit of zero pressure. That is, equating the ideal gas term in Eq. (9) in bulk and confinement, we see that, in the limit of $\tilde{P} \rightarrow 0$ that $\rho = G \tilde{\rho} = G \beta \tilde{P}$. We note that Henry's constant is often given in

terms of the specific adsorption Γ , defined by

$$\Gamma A = \int_V d\mathbf{r} (\rho(\mathbf{r}) - \tilde{\rho}) \quad (10)$$

where $\rho(\mathbf{r})$ is the inhomogeneous density profile, $\tilde{\rho}$ is the density of a bulk fluid in equilibrium (i.e., at the same chemical potential) as the confined fluid, V is a volume encompassing the confined fluid, and A is surface area of the system. Taking the limit $\tilde{\rho} \rightarrow 0$, we see that $\Gamma A = V(\rho - \tilde{\rho}) \rightarrow V(G - 1) = K_H \tilde{\rho}$, which defines Henry's constant K_H . Again, the exact definitions of V and A depend on the choice of dividing surface. We circumvent this by only considering specific adsorption per volume $\Gamma A/V$ below.

The entropy per particle, s , can be determined directly from differentiating the Helmholtz free energy, and is given by

$$s/k_B = \beta \left(\frac{\partial \beta f}{\partial \beta} \right)_{N,V} - \beta f \quad (11)$$

which, when applied to Eq. (8) leads to

$$\begin{aligned} s^{\text{ig}}/k_B &= -\frac{\beta}{G} \frac{\partial G}{\partial \beta} - \ln[\rho \Lambda^3/G] + 5/2, \\ s^{\text{ex}}/k_B &= \sum_{n=2} \frac{1}{n-1} \left[\beta \frac{\partial B_n}{\partial \beta} - B_n \right] \rho^{n-1}, \end{aligned} \quad (12)$$

where $\partial G/\partial \beta = -\int d\mathbf{r}_i \phi(i)g(i)/V$, and it is implicit that all derivatives are at constant V . Taking the derivative of Eqs. (6), we have

$$\frac{\partial B_n}{\partial \beta} = (1-n) \frac{\partial b_n}{\partial \beta} - \frac{\partial R_n}{\partial \beta}, \quad (13a)$$

$$\begin{aligned} \frac{\partial R_n}{\partial \beta} &= \sum_{\mathbf{m}} \left[m! B_m \left(\prod_{i=1}^n \frac{(i b_i)^{m_i}}{m_i!} \right) \right. \\ &\quad \left. \times \left(\frac{1}{B_m} \frac{\partial B_m}{\partial \beta} + \sum_{k=1}^n \frac{m_k}{b_k} \frac{\partial b_k}{\partial \beta} \right) \right], \end{aligned} \quad (13b)$$

subject to the constraints of Eq. (6c), and

$$\begin{aligned} \frac{\partial b_n}{\partial \beta} &= -b_n \frac{n}{G} \frac{\partial G}{\partial \beta} + \int d\mathbf{r}^n \left[\prod_{i=1}^n g(i) \right. \\ &\quad \left. \times \left(-\gamma(\mathbf{r}^n) \sum_{i=1}^n \phi(i) + \frac{\partial \gamma(\mathbf{r}^n)}{\partial \beta} \right) \right]. \end{aligned} \quad (14)$$

In the case of a bulk fluid, we can differentiate Eq. (7) directly (which leads to the same expression, except the integral is over $\partial\Gamma(\mathbf{r}^n)/\partial\beta$ instead of $\Gamma(\mathbf{r}_n)$).

The density profile $\rho(\mathbf{r})$ is obtained from the functional derivative of the Helmholtz free energy with respect to external field

$$\begin{aligned} \rho(\mathbf{r}) &= \left(\frac{\delta f N}{\delta \phi(\mathbf{r})} \right)_{\beta, N} \\ &= \rho g(\mathbf{r}) + V \beta^{-1} \sum_{n=2} \frac{1}{n-1} \frac{\delta B_n}{\delta \phi(\mathbf{r})} \rho^n \\ &= \sum_{n=1} B_n(\mathbf{r}) \rho^n, \end{aligned} \quad (15)$$

which implicitly defines what we term the density-profile virial coefficients $B_n(\mathbf{r})$, which depend on position \mathbf{r} . Taking the derivative of Eqs. (6), leads to an expression exactly analogous to Eq. (13) (replacing the β derivatives with $\phi(\mathbf{r})$ functional derivatives). In addition, the functional derivative of b_n is given by

$$\frac{\delta b_n}{\delta \phi(\mathbf{r})} = -n\beta V^{-1} g(\mathbf{r}) [b_n(\mathbf{r}) - b_n], \quad (16a)$$

$$n! b_n(\mathbf{r}) = \int d\mathbf{r}^{n-1} \gamma(\mathbf{r}, \mathbf{r}^{n-1}) \prod_{i=2}^n g(i), \quad (16b)$$

Note that by definition, $V b_n = \int d\mathbf{r}_1 g(1) b_n(\mathbf{r})$.

3. Relationship with Belleman's expansion

Here we discuss how Rowlinson's virial expansion presented above compares to the virial expansion of confined properties developed by Belleman [10, 11]. There are two main forms of Belleman's expansion: the surface tension and the confined density expansions. Both forms are expressed as expansions in terms of the density of a bulk fluid in equilibrium with the confined system. The coefficients from the two expansions are interrelated by a recursion relationship which also depends on the bulk coefficients \tilde{B}_n . While we can relate the Rowlinson coefficients to either the surface tension or confined density coefficients, here we only show the relationship to the surface tension expansion. The surface tension is defined by $\sigma A = \Omega - \tilde{\Omega}$, where A is the surface area and it is understood that quantities are at identical chemical potentials. It will be clearer to consider the excess surface tension $\sigma^{\text{ex}} = \sigma + K_{\text{H}}\tilde{P}/A$. The expansion of the σ^{ex} in terms of bulk density $\tilde{\rho}$ is given by [25]

$$-\beta\sigma^{\text{ex}}A = \sum_{n=2} W_n \tilde{\rho}^n, \quad (17)$$

where W_n are the Belleman expansion coefficients. Likewise, the surface tension is written in terms of the activity expansion by [25]

$$-\beta\sigma^{\text{ex}}A = \sum_{n=2} A_n \alpha^n, \quad (18)$$

where $A_n = V(b'_n - G\tilde{b}'_n)$ is the excess activity coefficient, and $b'_n = b_n G^n$. Substituting $\tilde{\rho} = \sum n\tilde{b}'_n \alpha^n$ into Eq. (17), expanding, and equating like powers of α in Eq. (18) leads to expressions for W_n in terms of b_n and \tilde{b}'_n . Therefore, the coefficients of both Belleman's and Rowlinson's expansion can be written in terms of b_n and \tilde{b}'_n . Of course, the coefficients W_n can be calculated directly by integrating the corresponding diagrams. While in theory the two series can be transformed into each other, numerical errors will be enhanced by this process compared to a direct calculation of the coefficients from their corresponding diagrams. Still, it is instructive to show the two expansions are easily related to each other.

This leads to a relevant question regarding when each series representation should be used. This depends on the nature of the system and properties of interest. The nature of Belleman's expansion is well suited to the study of a fluid near a single wall and to the study of hard particle fluids [25, 27]. Both of these advantages are due to the diagrams in Belleman's expansion having contributions primarily near the fluid-solid interface. This also means that for large pores (e.g., pores large enough to possess bulk-fluid in the center of the pore), Belleman's expansion would be preferable to Rowlinson's expansion, as the cluster integrals in Rowlinson's expansion have important contributions throughout the pore. However, for continuous fluid-solid potentials, contributions further from the interface will also be important. Also, the Belleman expansion has the added bonus of expressing some confined properties, like the average confined density and density profile, directly in terms of the bulk density. However, other thermodynamic properties, e.g., the Helmholtz free energies or Grand potential of the confined system, are not directly expressible as a function of the bulk density using the Belleman expansion alone. Calculating such properties with Belleman's expansion additionally requires a bulk-fluid equation of state (or bulk-fluid virial expansion). On the other hand, Rowlinson's expansion gives free energies directly as a function of confined density. In general, construction of isotherms of confined properties (e.g. confined density ρ) in terms of bulk properties other than bulk density (e.g., bulk pressure \tilde{P}), requires both the confined expansion and a bulk equation of state.

The Rowlinson's expansion has a clear conceptual advantage because it is more closely related to the bulk expansion than Belleman's expansion. The diagrams for b_n and \tilde{b}_n are exactly the same, save the factors of $g(\mathbf{r})$. Therefore, the calculation of Rowlinson's virial coefficients in bulk and confinement share much in common, and can utilize a common calculation algorithm. The similarities between the bulk and confined Rowlinson coefficients also gives a clearer picture to the interpretation of the coefficients. It is for these reasons that we focus on Rowlinson's expansion in this work.

4. Model fluids

We study four adsorbate-adsorbent systems of varying fluid-solid attractive strength. All systems considered have been studied via simulation previously, and thus abundant thermodynamic data is available. The systems are composed of a pure fluid confined in a single cylindrical pore of nominal pore radius R . The simplest system consists of hard spheres of diameter σ in a cylindrical hard-wall pore, which we denote as the HS system, and simulation data is taken from Ref. [30]. The other three systems are based on various gases adsorbed in attractive pores. All gases are modeled with Lennard-Jones (LJ) potentials with particle diameter parameter σ and energy parameter ϵ , truncated by a linear force shift at a cutoff distance r_{cut} , and all gas-adsorbent interactions are modeled using smeared potentials. The first attractive system mimics argon adsorption in a multiwalled carbon nanotube (CNT). This system has been studied with $r_{\text{cut}}/\sigma = 2.5$ and 6.0 , in Refs. [31, 32], respectively, and we denote these two systems as CNT[2.5] and CNT[6.0]. The next attractive system models argon adsorption in a cylindrical pore bored out of solid carbon dioxide. This system used has been studied with $r_{\text{cut}}/\sigma = 4.0$ in Ref. [32], and we denote this system as CO₂. The last system mimics methane adsorption in a silicate MCM-41 adsorbent. This system has been studied with $r_{\text{cut}}/\sigma = 4.0$ in Ref. [33], and we denote this system as MCM41. Further details regarding the specifics of each system, can be found in the references cited.

The nominal pore volume $V = \pi R^2 L$, where L is the pore length, defines the density $\rho = N/V$, where N is the number of fluid particles in the system. However, the geometric meaning of the pore radius R , and likewise particle size σ , are not equivalent across the systems due to the smooth fluid-solid and fluid-fluid interactions present in the attractive systems. For this reason, we instead use the effective pore radius R_{eff} defined in Ref. [32], and the Barker-Henderson particle diameter [34] σ_{BH} . These can be viewed as hard-sphere like measures for pore and particle size. Indeed, the effective parameters are identical to the nominal parameters for the HS system. We denote values scaled by these effective values with an asterisk. The reduced effective density is $\rho^* = \rho_{\text{eff}} \sigma_{\text{BH}}^3$, where $\rho_{\text{eff}} = N/V_{\text{eff}}$ and $V_{\text{eff}} = \pi R_{\text{eff}}^2 L$ are the effective density and

volume, respectively. The reduced effective pore radius is $R^* = R_{\text{eff}}/\sigma_{\text{BH}}$. Likewise, $G^* = \int d\mathbf{r}_1 g(1)/V_{\text{eff}}$. All properties presented will be dimensionless quantities such as $\beta\Omega/N = \sum_n B_n^* \rho^{*n-1}$, $\rho(r)\sigma_{\text{BH}}^3 = \sum_n B_n^*(r)\rho^{*n}$, $\beta\mu^{\text{ex}}$, etc. Note that in the bulk limit, $R \rightarrow \infty$, effective and bare quantities are identical, e.g., $\tilde{B}_n^* = \tilde{B}_n$.

We investigate the supercritical reduced temperatures $T^* = k_{\text{B}}T/\epsilon = 1.5$ for the LJ fluids and unit temperature for the HS fluid. We consider a number of pore sizes, with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 2.5, 3.5, 5.5,$ and 7.5 , but concentrate in the main text on systems with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$. Effective parameters and G^* values for these systems are given in Table 1. Values at the other pore sizes are given in Supporting Information (SI). A comparison of the external field for the various systems considered is shown in Figure 1. Clearly, the systems are ordered from least attractive to most attractive as $\text{HS} < \text{CO}_2 < \text{MCM41} < \text{CNT}$. This is also reflected in the values of G^* shown in Table 1.

5. Mayer-sampling Monte Carlo simulations

We calculate the virial coefficients using the MSMC method to sample the cluster integral in Eq. (2). We closely follow the method described in Ref. [27], which used the overlap-sampling formulation of MSMC to calculate the virial coefficient of hard spheres in slit-pore confinement, but highlight some minor changes needed for the systems considered in this work. The simulation technique requires sampling both a target and a reference system. The reference system is composed of the same number of hard spheres as the target system, and the same external field as the target system, but the external field only interacts with the first particle. In the case of the HS system, the reference hard spheres have the same diameter as the target system. In the case of the attractive systems, the reference hard-spheres have a diameter of 1.5σ , as suggested by a previous MSMC study of bulk LJ fluids [24].

The value of the connected diagrams $\gamma(\mathbf{r}^n)$ is calculated using the Wheatley algorithm [35]. The derivative $\partial b_n/\partial\beta$ is also calculated during the simulations. For this, we calculate $\partial\gamma(\mathbf{r}^n)/\partial\beta$ by differentiating the expression for $\gamma(\mathbf{r}^n)$ (see SI Sec. S-A). Likewise, we calculate $b_n(\mathbf{r})$ during the simulation by averaging over a cylindrical shell of width Δr .

For all system parameters considered, we calculate the virial coefficients up to order $n = 5$. We performed at least 20 independent simulations and each target simulation sampled at least 10^9 configurations. Each simulation was block averaged to give 40 property estimates. These estimates were combined across the independent simulations and then sampled via bootstrapping (i.e., sampling with replacement) to give 4000 estimates. These were then used to estimate 95% confidence intervals. For the HS system, we use the analytic expression for the virial coefficient at $n = 2$ presented in Ref. [29]. We note that the above algorithm converged quickly (within about 10000 Monte Carlo steps) for the pores considered in this study. Because the cluster integrals in Rowlinson’s expansion have important contributions from configurations throughout the pore, the computational cost grows with pore size. As discussed above, for sufficiently large pores, the above algorithm may converge slowly. For this reason, for sufficiently large pores (we estimate this to be $R/\sigma \gtrsim 15$), the algorithm of Refs. [25, 27] could be used to calculate Belleman’s virial coefficients, which have import contributions primarily near the fluid-solid interface. However, for the pore sizes considered in this work, we expect that the above algorithm to calculate Rowlinson’s virial coefficients will have a similar computational cost as the algorithm of Refs. [25, 27] to calculate Belleman’s virial coefficients.

6. Results

6.1. *Thermodynamic properties*

The MSMC simulation results for the virial coefficients and their temperature derivatives of the various systems considered with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ are presented in Table 2. We note that the uncertainties grow markedly with the coefficient order n , due to the increased complexity of the graphs involved, and the fact that B_n is calculated from the simulated values of $b_{k \leq n}$ via Eqs. (6b) and (13). Results for the other pore sizes considered are given in the SI. We note that all the virial coefficients of the HS system are positive, while those of the attractive systems are both positive and negative. Interestingly, for the attractive systems in Tab. 2, the rank order of the virial coefficients tend to follow the rank order of the strength of the fluid-solid attraction.

In other words, for a given order n , B_n^* tends to increase with the strength of the fluid-solid interaction. While this generally holds across pore sizes for order $n = 2$, there are cases where this ordering breaks down for orders $n > 2$ (see SI). We discuss the implications of this ordering further in Section 7.

We compare the values of the grand potential per particle, excess chemical potential, and excess entropy from simulation and the truncated virial expansion, via Eqs. (4), (9), and (12), respectively, for the systems with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ in Fig. 2. Note that we refer to a series truncated at order n as an n -th order series or expansion below, where Henry’s law corresponds to a series truncated at first order. To approximate the density range over which a series converges, we used the following procedure. We consider the difference $\Delta X_n(\rho^*) = |X_{\text{sim}}(\rho^*) - X_{\text{vir},n}(\rho^*)|$, which is the absolute difference between some property X from simulation and predicted from the virial expansion at order n . We then define the value $\rho_{X,n}^*$ as the minimum observed density for which $\Delta X_n(\rho^*) > 0.025$. We then consider a series as converged with respect to property X at order n for densities $\rho^* < \rho_{X,n}^*$. Values for $\rho_{X,n}$ with $X = \beta\Omega$, $\beta\mu$, and s for systems with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ are given in Table 3. Below, unless stated otherwise, we use the shorthand $\rho_{X,n}^*$ to refer to all properties X considered. By definition, replacing any of these properties X with its corresponding excess value would lead to the same result. We note that while the exact value of $\rho_{X,n}^*$ depends on the property X , the qualitative nature does not. We discuss this further below. Results at the other pores sizes can be found in the SI.

For the HS system, we see that the thermodynamics are captured very well by the virial expansion. As shown in Table 3, $\rho_{X,n}^*$ grows systematically with n for all properties X , with the fifth order series converging up to densities $\rho_{X,5}^* \approx 0.6$ for $X = \beta\Omega$ and $\beta\mu$, and $\rho_{s,5}^* \approx 0.8$. For the attractive systems, $\rho_{X,5}^* \approx 0.3$. We also observe that for these attractive systems, unlike for the HS system, the values of $\rho_{X,n}^*$ do not increase systematically with n . Going from first to second order, $\rho_{\beta\Omega,n}^*$ increases by approximately an order of magnitude for the CO₂ and HS systems, but changes little for the CNT[2.5] and MCM41 systems. In fact, $\rho_{\beta\Omega,1}^* > \rho_{\beta\Omega,2}^*$ for the MCM41 system. This suggests that, for the CNT[2.5] and MCM41 systems, that first order effects dominate at low densities. For all systems, $\rho_{X,n}^*$ increases greatly (by approximately

a factor of 2) going from second to third order, but increases much less, or not at all, going to higher orders for the attractive systems. For example, for the MCM41 system, there is little difference in $\rho_{X,n}^*$ from third to fifth order. We also observe for the CO₂ system that $\rho_{\beta\Omega,5}^* < \rho_{\beta\Omega,4}^*$, and likewise for $X = \beta\mu$. This latter effect may be due to errors in the calculated value of B_5^* , but this trend exists across pore sizes for this particular system (see SI). This is similar to the poorly converging virial expansion of bulk inverse power potential fluids, with low “hardness” parameters [36, 37]. For these systems, like the CO₂ system, the sign of the virial coefficient alternates and the magnitude of the virial coefficient grows with increasing order n . We also observe that for the CO₂ and CNT[2.5] systems, that $\rho_{s,2}^* > \rho_{s,n>2}^*$. This is due to the actual entropy being nearly linear over a broad range of densities for these systems. These trends are generally observed at the other pore sizes considered (see SI).

6.2. Isotherms

Typically, when studying the adsorptive characteristics of a system, one investigates isotherms of confined properties as a function of bulk pressure, density, or chemical potential. For the virial expansion investigated in this work, it is most straightforward to construct adsorption isotherms as a function of chemical potential. We construct isotherms of the confined density ρ^* and the excess specific adsorption $\Gamma^{\text{ex}} = \Gamma - K_{\text{H}}\tilde{\rho}/A$ as functions of chemical potential. The former is the total adsorption and the latter is the excess specific adsorption relative to the Henry’s law approximation. For the virial expansion estimates, these are constructed by calculating the chemical potential at a given confined density using Eq. (9). For Γ^{ex} , we calculate the $\tilde{\rho}(\mu)$ by interpolating the bulk simulation data at the chemical potential predicted by the virial expansion.

Excess specific adsorption is an especially relevant quantity for this study, as non-zero values of Γ^{ex} indicate, by definition, deviations from Henry’s law. While not shown, we note that the complete specific adsorption Γ is negative for the HS systems, and positive for all other systems. That is, HS pores contain less dense fluid and attractive pores contain more dense fluid than bulk fluid at the same chemical potential and volume corresponding to each pore (see Eq. (10)). However, the excess

specific adsorption shows the opposite behavior. This is due the definition of Γ^{ex} . While the attractive pores have positive Γ , they have less specific adsorption than Henry's law predicts.

The comparison of these isotherms from simulation and the virial expansion for the systems considered at $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ are shown in Fig. 3. We note that the total adsorption isotherms can be compared directly to the second row of plots in Fig. 2, where μ^{ex} is the chemical potential less the ideal gas term. Comparing Figs. 2 and 3 in this way, we see that the virial prediction of the total isotherm agrees with simulation data over the same confined density range $\rho_{\beta\mu,n}^*$ given in Table 3. Therefore, all the observations made regarding the confined thermodynamic properties likewise apply to the total isotherms. For example, the fifth order series agrees with the simulation data up to $\rho^* \approx 0.6$ for the HS system, and $\rho^* \approx 0.3$ for the attractive systems. We again observe that the density range over with the virial expansion agrees with simulations for the HS system increases systematically with order, for the HS system, and for the attractive systems increases greatly from first to third order but does not change much going to higher orders. This drastic improvement going from second to third order is especially evident in Γ^{ex} , where the third order series agrees almost perfectly with simulation. However, this is most likely fortuitous, as $\Gamma^{\text{ex}}(\mu)$ obscures some of the details seen in the $\rho^*(\mu)$. For example, the change of curvature $\rho^*(\mu)$ for the CNT[2.5] system near $\beta\mu \approx -5$ is not apparent in the $\Gamma^{\text{ex}}(\mu)$ isotherm. Still, it is quite remarkable how well $\Gamma^{\text{ex}}(\mu)$ is predicted at third order for all the attractive systems. We found (see SI) that the third order virial expansion semi-quantitatively describes $\Gamma^{\text{ex}}(\mu)$ for all systems and pore sizes considered.

6.3. Density profiles

The MSMC simulation results for the density-profile virial coefficients $B_n^*(r)$ for the various systems considered with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ are presented in Figure 4. Recall from Eq. (15) that $B_n^*(r)$ is the order n contribution to the virial expansion of the density profile, and as such, gives a measure of how n -body interactions impact the density profile. As in the case of B_n^* , the uncertainties in $B_n^*(r)$ grow with the coefficient order. Results for the other pore sizes considered are given in the SI. Focusing on $n \leq 2$, we

note that the behavior of $B_n^*(r)$ in the mildly attractive MCM41 system falls between that of the weakly attractive CO₂ system and the strongly attractive CNT[2.5] system. We also note that the behavior of the HS system is very different than the attractive systems. In Section 7 we will further interpret these characteristics of $B_n^*(r)$.

Next, we examine the density profiles as predicted by Eq. (15). First, we consider the HS system, shown in Fig. 5. Again, as density is increased, higher order terms are required for the series to converge. At $\rho^* = 0.1, 0.2,$ and $0.3,$ third, fourth and fifth order expansions converge to the simulations data, respectively. At $\rho^* = 0.3$ we see that, while the simulation data agree with the fifth order expansion within error bounds, there does appear to be a deviation at the center of the pore. This becomes clearer as the density is further increased to $\rho^* = 0.4,$ where again the fifth order expansion agrees with simulations within error bounds, but the deviation is more pronounced (the mean prediction overestimates the simulated density profile by up to a factor of two near the center of the pore). Finally, at $\rho^* = 0.5,$ we see that the fifth order series fails to converge to the simulated profile. Comparing these results with the values of $\rho_{X,n}^*$ in Table 3 shows that the density range over which the virial expansion agrees with simulations at a given order n is smaller for the density profile than for other thermodynamic properties X . For example, at $\rho^* = 0.2$ at third order ($\rho_{\beta\Omega,3}^* = 0.235$), we see that the third order series for $\rho^*(r)$ accurately captures the first layer, but fails to agree with the second layer, which is small but visible at this density. However, the fourth order series agrees well with simulation results. In general, it appears that to achieve the same level of accuracy, the virial prediction of $\rho^*(r)$ requires an extra series term compared to the virial prediction of thermodynamic properties. This is not surprising, as the density profile contains much more detailed information than the pore-averaged thermodynamic properties considered in Table 3. It is very possible that the virial expansion misses some details of the density profile, while still capturing the pore-averaged thermodynamic properties well.

Next, we consider the density profiles in the attractive systems. These profiles are shown in Fig. 6. We first consider the highly attractive CNT[2.5] system. We see that the density profile is accurately captured by the first order expansion up to density of $\rho^* \approx 0.15$. In fact, the film layer is well captured at first order for all values of ρ^*

shown. This is not surprising for such a strongly attractive system, where the fluid-solid interactions dominate at low density. A second layer, interior to the film, develops at the higher densities. Figure 7 shows the density profiles zoomed in on this second layer. Notice that the second layer is predicted progressively better with increasing order. It is interesting that even at the lowest density, the fifth order expansion is needed to accurately capture this second layer, indicating that the second layer depends on many body effects. In general, we find that the virial expansion tends to under predict the second layer density profile as the pore density increases. The magnitude of the underprediction also increases with pore density. These trends indicate that the series requires higher order terms to converge.

Next, we consider the density profiles of the weakly attractive CO₂ system, also shown in Figs. 6 and 7. For this system, particles are located in the first and second layer at all densities shown. The peak density in the first layer of CO₂ system is approximately 30% of that in the CNT[2.5] system at similar density (note the different scales of the vertical axes of Fig. 6) due to the weaker fluid-solid interactions. However, the peak density in the second layer is roughly an order of magnitude larger in the CO₂ system than in the CNT[2.5] system (see Fig. 7). We see that the first order expansion does not capture even qualitatively the density profile at $\rho^* \approx 0.15$, the lowest density considered. Therefore higher order effects are needed to capture the first layer even at low, but finite, densities for the CO₂ system. At $\rho^* \approx 0.15$, the profile is well captured by the second order virial expansion. At $\rho^* \approx 0.2$ and 0.25 , the profile is well described by the fifth order expansion. At $\rho^* \approx 0.3$, while the first layer is well described by the expansion at $n = 5$, we see that the expansion under predicts the profile in the second layer (see Fig. 7). We also note that, for all densities, the virial expansion of order $n \geq 4$ is required to accurately capture the second layer of the density profile, again indicating that this layer depends on many body effects.

Lastly, we consider the MCM41 system. The peak height in the first layer of the MCM41 system is similar to that in the CNT[2.5] system, and the peak height in the second layer is approximately 50% smaller than in the CO₂ system and approximately four times larger than in the CNT[2.5] system, at similar densities. That is, the mildly attractive MCM41 system shares characteristics with the weakly attractive CO₂ sys-

tem and the strongly attractive CNT[2.5] system. At the lowest density shown, the profile in the first layer is well captured at first order. Unlike the CNT[2.5] system, but like the CO₂ system, the first order expansion does not accurately capture the film layer at all considered densities. It systematically overpredicts the peak density in the film for $\rho^* > 0.15$. The second layer is well captured by the fifth order expansion for all densities considered (see Fig. 7), with lower order terms systematically underpredicting the simulation data.

7. Discussion

The main findings presented above hold across the different pore sizes considered, results for which are shown in Supporting Information. While there are some differences in the density range over which the series converge for the attractive systems, typically the fifth order series agrees with simulations roughly up to densities $\rho^* \approx 0.3$ for the attractive pores across all the properties investigated. Physically, fluid particles in these systems are located primarily in the fluid film layer adjacent to the pore wall in this density range, typically termed the film-formation regime. For the HS fluid, the virial expansion converges over a broader range of densities, (see above and SI). In many cases, the thermodynamics are accurately predicted up to $\rho^* \lesssim 0.6$ with the fifth order virial series, while the density profiles yielded by the fifth order series typically agree well with simulation data for $\rho^* \lesssim 0.4$. As can be seen in Fig. 5, differences in the density profile appear near the center of the pore at higher pore densities. For the HS systems, there are two possible reasons for the difference in the density range over which the thermodynamic and density-profile series agree with simulation results. The first is that the high density series prediction of thermodynamic properties is simply fortuitous. The other is that, because the center of the pore is such a small portion of the system, the differences in $\rho(r)$ at the center of the pore have little impact on the overall thermodynamics. Regardless, we can state that all properties of the HS system are well described by fifth order virial series up to $\rho^* \lesssim 0.4$, which is similar to what was found for hard spheres in slit-pore confinement [27].

In general, the virial expansion significantly improves upon Henry’s law. We do

note that for the attractive pores, the improvement to Henry’s-law-based (e.g., infinite-dilution) predictions from the virial series was minimal at second order, but significant at third order (See Table 3). For the purely repulsive HS and weakly attractive CO₂ systems, Henry’s law (i.e., series truncated at first order) agrees with simulations only in the infinite-dilution ($\rho^* \rightarrow 0$) limit. For the mildly attractive MCM41 and strongly attractive CNT[2.5] systems, Henry’s law predictions of grand potential, chemical potential, and isotherms (see Figs. 2 and 3) agree with simulations for densities $\rho^* \lesssim 0.1$. This is also the case for the density profiles of these systems (see Fig. 6). As discussed above, the fluid-solid interactions dominate the physics of these attractive systems at low densities. For this reason, Henry’s law, which takes into account only fluid-solid interactions, can be applied rather accurately over a density range beyond infinite-dilution limit. However, as observed in Fig. 7, accurate description of the second layer requires higher order expansion. Therefore, it appears that Henry’s law applies to cases where fluid is primarily located in the film layer. We also note that Henry’s law prediction of entropy only applies in the infinite-dilution limit for all systems, which is consistent with the expectation that detailed fluid structure cannot be captured by Henry’s law alone.

Figure 8 shows the dependence of the virial coefficients on pore size for the various systems considered. The bulk virial coefficients \tilde{B}_n^* correspond to the $R_{\text{eff}} \rightarrow \infty$ limit. We see that the purely repulsive HS system does not vary greatly with pore size, and thus the values of the confined virial coefficients are comparable to the bulk values. For the CO₂ system, the confined virial coefficients B_n^* vary slightly more with pore size than they do in the HS system, but they still do not vary much from their bulk values. In contrast, the values of B_n^* for the CNT[2.5] system are significantly different from their bulk values over the pore sizes studied, which suggest, unsurprisingly, that the effects of confinement are much greater for strongly attractive systems compared to weakly adsorptive systems. The impact of pore size on the mildly attractive MCM41 system is again somewhere between that of the CO₂ and the CNT[2.5] systems. One important note, which is unfortunately due to the parameters used in the original studies, is that the cutoff distance used in the different attractive systems complicates detailed analysis. The fluid-fluid interactions in CNT[2.5] system are somewhat less

attractive than the $r_{\text{cut}}/\sigma = 4.0$ fluid interactions of the CO₂ and MCM41 systems. However, the CNT[6.0] system is more like the $r_{\text{cut}}/\sigma = 4.0$ cases than the 2.5 cutoff of the CNT[2.5] system. Considering the second virial coefficient, we see that the CNT[6.0] system still shows higher deviation from its bulk value than the less attractive CO₂ and MCM41 systems, but the behavior of B_2^* for this system is quite different than for the CNT[2.5] system. Still, the general trend is that strong fluid-solid interactions lead to more variability of B_n^* with respect to their corresponding bulk values.

The qualitative ordering of the virial coefficients, where less attractive fluid-solid interactions lead to lower confined virial coefficient, runs counter to the typical understanding of the bulk second virial coefficient, \tilde{B}_2^* . We typically think of a more negative value of \tilde{B}_2^* as indicating strong attractions. However, we see that in the confined case, this does not hold. In fact, B_2^* for the strongly attractive CNT[2.5] system is actually positive. This is due to the dual contributions of the fluid-fluid and fluid-solid interactions to the second virial coefficient. Said another way, B_2^* in confinement is actually a three-body term, and therefore the closest analog is the bulk third virial coefficient which does not in general have a simple interpretation.

More meaning can be gleaned from investigating the values of $B_n^*(r)$. Note first the vertical guide lines displayed in Figs. 4, 5, and 6 at $x^* = (R_{\text{eff}} - r)/\sigma_{\text{BH}} = 1.2$ and 2.1. The first and second fluid layers (see Figs. 5 and 6) are approximately bound in the ranges $0 \lesssim x^* \lesssim 1.2$ and $1.2 \lesssim x^* \lesssim 2.1$, respectively. We see that there are distinct peaks in $B_n^*(r)$ in the first and second layers of $\rho(r)$. This identification will aid the interpretation of the contributions of $B_n^*(r)$ to $\rho(r)$. For the CO₂ system, $B_2^*(r)$ has a negative peak in the first layer, and a positive peak in the second layer. On the other hand, $B_2^*(r)$ for the CNT[2.5] system has a comparatively small negative peak in the first layer, and no visible positive peak in the second layer. For the mildly attractive MCM41 system, the behavior $B_2^*(r)$ is between that of the CO₂ and CNT[2.5] systems: it displays a negative first peak, and positive second peak, both of which are bounded by the weakly attractive CO₂ and strongly attractive CNT[2.5] systems. The interpretation of the higher order terms is more complicated, but still informative. Across all orders, the magnitude of $B_n^*(r)$ is large for the CO₂ system and small for the CNT[2.5] system. For the CNT[2.5] system, this provides an explanation for why the first order

series was successful in describing $\rho(r)$ over a broad range of ρ^* : the higher order terms are small perturbations to the infinite-dilution limit. We also see that across orders, the characteristics of $B_n^*(r)$ for the MCM41 system mostly fall somewhere between those of the CO₂ and CNT[2.5] systems. In particular, $B_n^*(r)$ is negative and sharp for both the MCM41 and CNT[2.5] systems at all orders. On the other hand, the magnitude of $B_n^*(r)$ in the second layer for the MCM41 system for $n \geq 3$ is more similar to that of the CO₂ system, although the sign is different between the two systems for $n \geq 4$. That is, the degree of correction in the second layer is greater for the CO₂ and MCM41 systems compared to the highly attractive CNT[2.5] system. Lastly, we note that the behavior of $B_n^*(r)$ for the HS system is completely different than for the attractive systems. Somewhat surprisingly, the largest differences appear to be between the HS system and the weakly attractive CO₂ system. This emphasizes the important, and sometimes subtle, role that the attractions play in dictating adsorption thermodynamics.

8. Conclusions

We have investigated the confined density virial expansion of adsorptive systems up to fifth order. We find that the virial expansion truncated at fifth order is valid for effective densities $\rho^* \lesssim 0.3$ for attractive systems. For purely repulsive HS systems, the fifth order expansion is valid for $\rho^* \lesssim 0.4$ for density profiles, and $\rho^* \lesssim 0.6$ for thermodynamic properties. This represents a significant increase in the predictive density range compared to that based on the infinite-dilution (Henry's law) limit. We find that for attractive systems, the range of applicable densities corresponds to particles being primarily near the fluid-solid interface.

Interestingly, we find that the value of the second order virial coefficient cannot be interpreted as a measure of attractive strength in confinement. In fact, we find the weakly attractive systems have a lower value of B_2 than strongly attractive systems. This suggests that the virial expansion can be interpreted as a perturbation of the infinite-dilution adsorbate limit, which will depend upon the strength of the fluid-solid interaction. This work leads to a number of open questions. One question is

whether higher order coefficients will greatly extend the density range over which in the virial expansion converges. This does seem to be the case for the HS system, where the density range over which the series converges grows approximately linearly with expansion order. However, this is not the case for attractive systems. For such systems, we find that adding higher order virial terms leads to a marginal increase in the density range over which the virial expansion can describe properties accurately. Moreover, for the mildly attractive system, we observed that the virial expansion shows signs of poor convergence. Given that computational expense increases with coefficient order, we see little use in exploring this further for attractive systems. On the other hand, it is quite easy to calculate the virial coefficient to third order (on the order of minutes for B_2 and an hour for B_3). Given some of the insights gleaned from the coefficients at low order, the virial expansion still has use in describing adsorptive thermodynamics. In particular, the virial coefficients might be useful for performing corresponding states analysis for confined systems. That is, matching values of Henry's law constant and B_2 might be indicative of similar properties or behavior. Given the increased interest in machine learning, another possible application involves the use of virial coefficients as descriptive parameters to building ML models. We hope to address these questions in future studies.

Supporting Information

See Supporting Information for further details on the virial expansion, and results for other pore sizes not considered in main text.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Table 1.: Values of system parameters and effective parameters for systems with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$.

	R/σ	T^*	$\sigma_{\text{BH}}/\sigma$	$R_{\text{eff}}/\sigma_{\text{BH}}$	G^*	$(\partial \ln G^*/\partial \ln \beta)$
HS	3.5	1.0	1.0000	3.500	0.735	0
CO ₂	4.0	1.5	1.0001	3.664	2.917	1.649
MCM41	4.0	1.5	1.0001	3.701	13.651	4.075
CNT[2.5]	3.99	1.5	1.0003	3.552	111.203	6.470

Table 2.: Virial coefficients and temperature derivatives of virial coefficients for the systems considered with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$. Note that values have been normalized relative to the effective density $\rho_{\text{eff}}\sigma_{\text{BH}}^3$. For example, $B_n^* = B_n[\sigma_{\text{BH}}^{-3}V_{\text{eff}}/V]^{n-1}$, etc. Values in parenthesis represent the 95% confidence interval in the right most digit(s).

System	R/σ	T^*	n	B_n^*	$(\partial B_n^*/\partial \ln \beta)$
HS	3.5	1	2	2.49519	0
			3	3.3089(25)	
			4	3.21(7)	
			5	4.2(1.2)	
CO ₂	4.0	1.5	2	-1.03402(19)	-3.0533(4)
			3	2.446(3)	5.309(12)
			4	-3.27(6)	-9.28(28)
			5	-4.1(1.0)	-51(6)
MCM41	4.0	1.5	2	-0.3527(4)	-3.0334(9)
			3	5.424(8)	10.204(25)
			4	-0.27(14)	1.2(6)
			5	-1.7(2.2)	-10(12)
CNT[2.5]	3.99	1.5	2	0.4521(4)	-2.6583(6)
			3	5.536(7)	5.156(19)
			4	5.05(10)	-7.9(4)
			5	21.5(1.4)	20(6)

Table 3.: Values of $\rho_{X,n}^*$ for systems with $R_{\text{eff}}/\sigma_{\text{BH}} \approx 3.5$ and $X = \beta\Omega$, $\beta\mu$, and s .

X	System	R/σ	T^*	$n=1$	2	$\rho_{X,n}^*$ 3	4	5
$\beta\Omega$	HS	3.50	1.0	0.020	0.120	0.235	0.355	0.610
	CO ₂	4.00	1.5	0.060	0.161	0.286	0.328	0.286
	MCM41	4.00	1.5	0.140	0.099	0.280	0.286	0.292
	CNT	3.99	1.5	0.063	0.095	0.177	0.202	0.328
$\beta\mu$	HS	3.50	1.0	0.015	0.100	0.220	0.335	0.615
	CO ₂	4.00	1.5	0.030	0.131	0.244	0.316	0.274
	MCM41	4.00	1.5	0.134	0.082	0.269	0.280	0.286
	CNT	3.99	1.5	0.044	0.076	0.164	0.196	0.335
s	HS	3.50	1.0	0.025	0.175	0.350	0.500	0.800
	CO ₂	4.00	1.5	0.030	0.405	0.238	0.298	0.316
	MCM41	4.00	1.5	0.023	0.140	0.245	0.251	0.245
	CNT	3.99	1.5	0.019	0.297	0.284	0.240	0.234

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